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Atty. Dkt. No. 023174-0166

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Koji HAGIYA
Title: FLUORINATING AGENT AND METHOD
FOR PRODUCING FLUORINE-
CONTAINING COMPOUND USING THE
SAME
Appl. No.: 10/583,608
International Filing Date: 12/21/2004
371(c) Date: 6/20/2006
Examiner: Rei Tsang Shiao
Art Unit: 1626
Confirmation Number: 2628

CERTIFIED ENGLISH TRANSLATION OF PRIORITY DOCUMENTS
TRANSMITTAL

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Further to Applicant's claim of priority under 35 U.S.C. § 119 from foreign applications, Japanese Patent Application Nos. 2003-429133, 2003-429134, both filed December 25, 2003, Japan Patent Application No. 2004-068703, filed March 11, 2004, and Japan Application No. 2004-182102, filed June 21, 2004, Applicant submits herewith a Certified English Translation of said original foreign applications.

Respectfully submitted,

Date February 12, 2009

By [Signature]

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D E C L A R A T I O N

I, Kazuya MINAMISAKA, a national of Japan, c/o Sumitomo Chemical Intellectual Property Service, Limited, 5-33, Kitahama 4-chome, Chuo-ku, Osaka 541-8550, Japan, declare that to the best of my knowledge and belief the attached is a full, true, and faithful translation into English made by me of the of Japanese Patent Application Number 2003-429133.

Signed this *30th* of January, 2009

Kazuya Minamisaaka

Kazuya MINAMISAKA

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: December 25, 2003

Application Number: 2003-429133

[ST. 10/C]: [JP2003-429133]

Applicant(s): Sumitomo Chemical Company, Limited

November 10, 2004

Commissioner,

Japan Patent Office

Hiroshi OGAWA (SEAL)

No.2004-3101392

[Name of Document] Request for Patent

[Reference Number] P156564

[Date of Submission] December 25, 2003

[Address] Commissioner of the Patent Office

[International Patent Classification] C07D233/58

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[Indication of Fee]

[Prepayment Resister Number] 010238

[Amount of Payment] 21,000 yen

[List of Submitted Materials]

[Name of Material] Scope of claims for patent 1

[Name of Material] Specification 1

[Name of Material] Abstract 1

[Number of General Power] 0212949

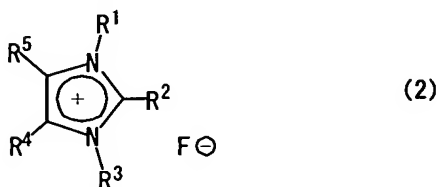
[Necessity for Proof] Yes

[Title of Document] SCOPE OF CLAIMS FOR PATENT

[Claim 1]

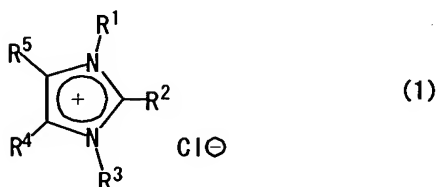
A method for producing an alkyl-substituted imidazolium fluoride represented by the formula (2):

[Formula 2]



wherein R^1 and R^3 are the same or different, and each represents an optionally substituted alkyl group, R^2 , R^4 and R^5 are the same or different, and each represents a hydrogen atom or an optionally substituted alkyl group, which comprises reacting an alkyl-substituted imidazolium chloride represented by the formula (1):

[Formula 1]



wherein R^1 , R^2 , R^3 , R^4 and R^5 are the same meanings as defined above,

with a silver fluoride.

[Claim 2]

The method according to Claim 1, wherein the silver fluoride is a monovalent silver fluoride.

[Title of Document] SPECIFICATION

[Title of the Invention] Method for producing an alkyl-substituted imidazolium fluoride

[Technical Field]

[0001]

The present invention relates to a method for producing an alkyl-substituted imidazolium fluoride.

[Background Art]

[0002]

Alkyl-substituted imidazolium fluorides are important compounds as a fluorinating agent and electrolyte raw materials. As the methods for producing the alkyl-substituted imidazolium fluoride, for example, a method comprising reacting an alkyl-substituted imidazolium chloride with hydrogen fluoride (e.g. Non-patent document 1), a method comprising reacting an alkyl-substituted imidazolium carbonate with ammonium fluoride (e.g. Patent document 1) or the like has been known. However, highly corrosive and toxic hydrogen fluoride was used in the former method, and the yield was low in the latter method, and therefore, they have been desired to improve as industrial methods.

[0003]

[Patent document 1] JP 2003-335734 A

[Non-patent document 1] J. Fluorine. Chem., 99, 1 (1999)

[Disclosure of the Invention]

[Problems to be solved by the Invention]

[0004]

Under these circumstances, the present inventor has

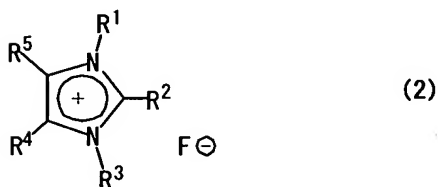
intensively studied in order to develop a more industrially advantageous method for producing an alkyl-substituted imidazolium fluoride and, as a result, he has found that an alkyl-substituted imidazolium fluoride can be easily produced in a high yield by reacting an alkyl-substituted imidazolium chloride with a silver fluoride, thereby completing the present invention.

[Means for Solving the Problems]

[0005]

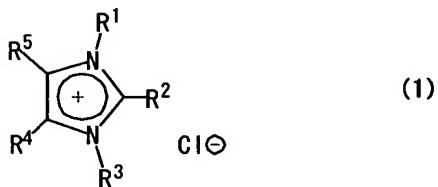
That is, the present invention is to provide a method for producing an alkyl-substituted imidazolium fluoride represented by the formula (2):

[Formula 2]



wherein R^1 and R^3 are the same or different, and each represents an optionally substituted alkyl group, R^2 , R^4 and R^5 are the same or different, and each represents a hydrogen atom or an optionally substituted alkyl group, which comprises reacting an alkyl-substituted imidazolium chloride represented by the formula (1):

[Formula 1]



wherein R^1 , R^2 , R^3 , R^4 and R^5 are the same meanings as defined

above,

with a silver fluoride.

[Effects of the Invention]

[0006]

According to the present invention, an alkyl-substituted imidazolium fluoride, which is an important compound as a fluorinating agent, an electrolyte raw material and the like, can be easily produced in a high yield from a highly available alkyl-substituted imidazolium chloride, and in this point, it is industrially advantageous.

[Best Mode for Carrying out the Invention]

[0007]

The present invention will be explained in detail below.

[0008]

In the alkyl-substituted imidazolium chloride represented by the formula (1) (hereinafter, simply referred to as the alkyl-substituted imidazolium chloride (1)) R^1 and R^3 are the same or different, and each represents an optionally substituted alkyl group, and R^2 , R^4 and R^5 are the same or different, and each represents a hydrogen atom or an optionally substituted alkyl group, in the formula.

[0009]

Herein, examples of the alkyl group include a straight chain, branched chain or cyclic C1-C20 alkyl group such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, an n-pentyl group, an n-decyl group, a cyclopropyl group, a 2,2-dimethylcyclopropyl group, a cyclopentyl group, a cyclohexyl group and a menthyl group. The alkyl group may be

substituted with a C1-C20 alkoxy group which may be substituted such as a methoxy group, an ethoxy group, an n-propoxy group, an isopropoxy group, an n-butoxy group, an isobutoxy group, a sec-butoxy group, a tert-butoxy group and a trifluoromethoxy group; a C6-C20 aryl group which may be substituted such as a phenyl group, a 4-methylphenyl group and 4-methoxyphenyl group; a C6-C20 aryloxy group which may be substituted such as a phenoxy group, a 2-methyphenoxy group, a 4-methyphenoxy group, a 4-methoxyphenoxy group and a 3-phenoxyphenoxy group; a C7-C20 aralkyloxy group which may be substituted such as a benzyloxy group, a 4-methylbenzyloxy group, a 4-methoxybenzyloxy group and a 3-phenoxybenzyloxy group; a fluorine atom; a C2-C20 alkylcarbonyl group which may be substituted such as an acetyl group and an ethylcarbonyl group; a C7-C20 arylcarbonyl group which may be substituted such as a benzoyl group, a 2-methylbenzoyl group, a 4-methylbenzoyl group and a 4-methoxybenzoyl group; a C8-C20 aralkylcarbonyl group which may be substituted such as a benzylcarbonyl group, a 4-methylbenzylcarbonyl group and a 4-methoxybenzylcarbonyl group; or a carboxyl group. Examples of the alkyl group substituted with the substituent include a fluoromethyl group, a trifluoromethyl group, a methoxymethyl group, an ethoxymethyl group and a methoxyethyl group.

[0010]

Examples of the alkyl-substituted imidazolium chloride (1) include 1,3-dimethylimidazolium chloride, 1,2,3-trimethylimidazolium chloride, 1,2,3,4-tetramethylimidazolium chloride, 1,2,3,4,5-pentamethylimidazolium chloride, 1-methyl-3-ethylimidazolium chloride, 1,2-dimethyl-3-ethylimidazolium

chloride, 1,3-diethylimidazolium chloride, 1-methyl-3-(n-propyl)imidazolium chloride, 1-methyl-3-(n-butyl)imidazolium chloride, 1,2-dimethyl-3-(n-butyl)imidazolium chloride, 1-methyl-3-(n-pentyl) imidazolium chloride, 1-methyl-3-(n-hexyl)imidazolium chloride, 1,3-dimethyl-2-ethylimidazolium chloride, 1, 3-dimethyl-2-(n-propyl)imidazolium chloride, 1,3-dimethyl-2-(n-butyl)imidazolium chloride, 1-dodecyl-2-methyl-3-dodecylimidazolium chloride, 1-dodecyl-2-methyl-3-benzylimidazolium chloride, 1-ethoxymethyl-3-methylimidazolium chloride and 1-trifluoromethyl-3-methylimidazolium chloride. These may form a complex with water, a polar inert solvent or the like.

[0011]

The alkyl-substituted imidazolium chloride (1) can be produced, for example, according to known methods such as a reaction of a substituted imidazole compound and an alkyl chloride (e.g. Tetrahedron, 59, 2253 (2003)).

[0012]

The alkyl-substituted imidazolium fluoride represented by the formula (2) (hereinafter, simply referred to as the alkyl-substituted imidazolium fluoride (2)) is obtained by reacting the alkyl-substituted imidazolium chloride (1) with a silver fluoride.

[0013]

The silver fluoride has a monovalent and divalent one. While both of them can be used, the monovalent silver fluoride is preferably used. Alternatively, while examples of the monovalent silver fluorides, two kinds thereof, silver(I) fluoride and silver subfluoride, silver(I) fluoride is more

preferably used from the viewpoint of cost.

[0014]

The used amount of the silver fluoride is usually 1 mole or more per 1 mole of the alkyl-substituted imidazolium chloride (1). While there is no specific upper limit, a range of about 1.0 to 1.1 moles is preferable for economic reasons.

[0015]

While the present reaction is usually carried out in the presence of an organic solvent, water or a mixture thereof, it may be carried out without using the solvent.

[0016]

Examples of the organic solvent include an ether solvent such as methyl tert-butyl ether and tetrahydrofuran; a nitrile solvent such as acetonitrile and propionitrile; an amide solvent such as dimethylformamide and dimethylacetamide; and a sulfur-containing solvent such as sulfolane and dimethylsulfoxide.

[0017]

While the used amount of the solvent is not particularly limited, it is usually about 100 parts by weight or less per 1 part by weight of the alkyl-substituted imidazolium chloride (1) in consideration of volumetric efficiency and the like.

[0018]

When the reaction temperature is too low, the reaction hardly proceed, and when the reaction temperature is too high, side reactions such as decomposition of a raw material or a product may proceed, and therefore, the practical reaction temperature is usually a range of about -20 to 200°C.

[0019]

The mixing order of the reaction agents is not particularly limited. For example, the silver fluoride may be added into the solution containing the alkyl-substituted imidazolium chloride (1) under the condition of the reaction temperature and they may be added in the inverted order. Alternatively, both agents and the solvent may be simultaneously mixed followed by adjusting the reaction temperature.

[0020]

The present reaction may be carried out at a normal pressure or under pressure.

[0021]

After completion of the reaction, silver chloride formed by the ion-exchange is usually precipitated in the system, and therefore, after removing this using a conventional method such as filtration and decantation, the alkyl-substituted imidazolium fluoride (2) can be isolated by concentrating the obtained solution. The isolated alkyl-substituted imidazolium fluoride (2) may be further purified by a means such as crystallization and column chromatography.

[0022]

The ending point of the reaction may be checked by a conventional analytical method such as ion chromatography, and when silver chloride is precipitated, the reaction may be finished at the point of confirming that the precipitate does not increase.

[0023]

Examples of the alkyl-substituted imidazolium fluoride (2) include 1,3-dimethylimidazolium fluoride, 1,2,3-

trimethylimidazolium fluoride, 1,2,3,4-tetramethylimidazolium fluoride, 1,2,3,4,5-pentamethylimidazolium fluoride, 1-methyl-3-ethylimidazolium fluoride, 1,2-dimethyl-3-ethylimidazolium fluoride, 1,3-diethylimidazolium fluoride, 1-methyl-3-(n-propyl)imidazolium fluoride, 1-methyl-3-(n-butyl)imidazolium fluoride, 1,2-dimethyl-3-(n-butyl)imidazolium fluoride, 1-methyl-3-(n-pentyl)imidazolium fluoride, 1-methyl-3-(n-hexyl)imidazolium fluoride, 1,3-dimethyl-2-ethylimidazolium fluoride, 1,3-dimethyl-2-(n-propyl)imidazolium fluoride, 1,3-dimethyl-2-(n-butyl)imidazolium fluoride, 1-dodecyl-2-methyl-3-dodecylimidazolium fluoride, 1-dodecyl-2-methyl-3-benzylimidazolium fluoride, 1-ethoxymethyl-3-methylimidazolium fluoride and 1-trifluoromethyl-3-methylimidazolium fluoride.

[Example]

[0024]

The present invention will be further illustrated in more detail by Examples. The present invention is not limited to these Examples.

[0025]

Example 1

Into an Erlenmeyer flask, 22 g of 1-methyl-3-(n-butyl)imidazolium chloride and 200 g of water were charged and dissolved. After 16.1 g of silver(I) fluoride and 120 g of water were charged into another Erlenmeyer flask to be dissolved, two aqueous solutions were mixed at 250C and the stirring was continued for 30 minutes at the same temperature. The crystalline precipitated after the reaction was filtered and washed with water. The filtrate and wash liquid obtained were joined and concentrated to obtain 24.5 g of colorless oil.

This oil was left at room temperature and then it crystallized. From the result of elementary analysis, the obtained crystalline was identified as 1-methyl-3-(n-butyl)imidazolium fluoride dihydrate. Yield: 100%.

[0026]

Elementary analytical value: C: 49.5, H: 9.9, N: 14.5, F: 9.2

Calculated value: C: 49.5, H: 9.9, N: 14.4, F: 9.8

¹H-NMR (δ ppm, DMSO-d₆, TMS standard): 0.90 (t, 3H), 1.25 (m, 2H), 1.72 (m, 2H), 3.88 (s, 3H), 4.19 (t, 2H), 7.79 (d, 2H), 10.1 (bs, 1H)

[0027]

Example 2

Into an Erlenmeyer flask, 5.2 g of 1-methyl-3-ethylimidazolium chloride and 50 g of water were charged and dissolved. After 4.54 g of silver(I) fluoride and 50 g of water were charged into another Erlenmeyer flask and dissolved, two aqueous solutions were mixed at 250C and the stirring was continued for 30 minutes at the same temperature. The crystalline precipitated after the reaction was filtered and washed with water. The filtrate and wash liquid obtained were joined and concentrated to obtain 6.4 g of colorless oil. The obtained oil was identified as 1-methyl-3-ethylimidazolium fluoride trihydrate from the result of the elementary analysis. Yield: 98%.

[0028]

Elementary analytical value: C: 39.5, H: 9.5, N: 15.5, F: 11.1

Calculated value: C: 39.1, H: 9.3, N: 15.2, F: 10.3

¹H-NMR (δ ppm, DMSO-d₆, TMS standard): 1.41 (t, 3H), 3.84 (s, 3H), 4.18 (q, 2H), 7.80 (d, 2H), 10.3 (bs, 1H)

[0029]

Reference Example (Use of the alkyl-substituted imidazolium fluoride (2) as a fluorinating agent)

Into a 50 mL flask equipped with a reflux condenser, 500 mg of 1-methyl-3-(n-butyl)imidazolium fluoride dehydrate and 284 mg of n-octyl paratoluenesulfonate were charged and the resulting mixture was stirred for 3 hours at 150°C. After cooling to room temperature, 5 g of ethyl acetate was added thereto and stirred. The mixture was separated to two layers by standing. The upper layer was analyzed by gas chromatography (internal standard method) to find out that the main product was 1-fluorooctane.

Yield: 98%. 1-Chlorooctane was not detected.

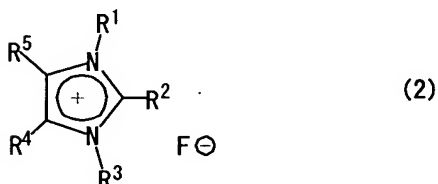
[Title of Document] ABSTRACT

[Abstract]

[Problem] It is to provide an industrially advantageous method for producing an alkyl-substituted imidazolium fluoride.

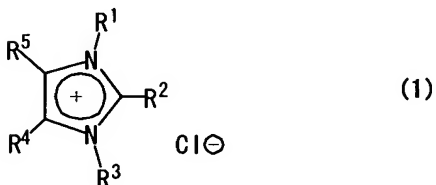
[Means to Solve] A method for producing an alkyl-substituted imidazolium fluoride represented by the formula (2):

[Formula 2]



wherein R^1 and R^3 are the same or different, and each represents an optionally substituted alkyl group, R^2 , R^4 and R^5 are the same or different, and each represents a hydrogen atom or an optionally substituted alkyl group, which comprises reacting an alkyl-substituted imidazolium chloride represented by the formula (1):

[Formula 1]



wherein R^1 , R^2 , R^3 , R^4 and R^5 are the same meanings as defined above,

with a silver fluoride.

[Selected Figure] None

Applicant History Information

Identification No.: [000002093]

1. Changing Date: August 28, 1990
[Reason for changing] Newly registration
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[Reason for changing] Name changing
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Name: Sumitomo Chemical Company, Limited